

the variable, let us imagine the microwave field strength to be held fixed at some suitably large value, and then inquire what theory predicts regarding ionization as a function of frequency when each electron initially has the same energy. Note that, with this change of variable, the transition to chaos will appear at a critical frequency rather than a critical field strength.

Typical theoretical results are presented in the figure where curves of classical and quantal ionization probabilities at a fixed time are plotted against the logarithm of a normalized microwave frequency. Below the critical frequency for the transition to classical chaos, both classical and quantal calculations predict the expected negligible absorption of microwave energy by the electron. But now come the surprises numerically discovered by Casati and colleagues. First, above the critical frequency both classical and quantal curves rise steeply together and then 'level off' onto a peak much wider and higher than the conventional photoelectric peak seen on the right in the figure. Second, when these previously unsuspected ionization peaks do begin to fall,

the quantum curve drops rapidly to zero long before the classical curve does. In essence, a frequency window is predicted inside which the classical electron ionizes whereas the quantum electron does not. Because here the electron is always initiated in a highly excited, 'semi-classical' state where quantal and classical results might be expected to agree, a remarkable question now arises. Can theory predict before the experiment whether the electron perceives itself as classical or quantal in this circumstance?

In this article I have sought to convey the excitement contained in the results of Casati *et al.*, the implications of which extend from applications of the new photoelectric peak to modifications in the foundations of physics resulting from chaos. But in a deeper sense, the true excitement of these papers lies not so much in their explicit content as in the tantalizingly brief glimpse they provide of competent scientists working on problems that count. □

*Joseph Ford is Regents' Professor of Physics at the Georgia Institute of Technology, Atlanta, Georgia 30332, USA.*

## Resonance ion spectroscopy

# Counting molecules one by one

Keith Boyer

TUNABLE lasers are rapidly entering the business of identifying, counting and concentrating atoms or molecules of specific chemical or isotope species, even in the presence of large backgrounds of very similar types such as neighbouring isotopes or chemical isomers. This technique has been dubbed resonance ionization spectroscopy (RIS), and it involves the ionization of free atoms or molecules, thus converting them to a detectable form through the absorption of two or more laser quanta. One of these quanta is resonant to provide selectivity; subsequent photons, which complete the ionization process, generally have different wavelengths. Some form of mass spectrometry is often used to increase selectivity, when because of its great sensitivity, the process has been called single-atom detection. The results described at a recent meeting\* show clearly that RIS is a rapidly maturing discipline of great importance.

Several outstanding accomplishments were reported at the symposium, but the most exciting was the extension of the technique to the identification and counting of both small and large complex molecules, despite the conclusion reached at the previous symposium in 1984 that molecules, as opposed to atoms, were not good candidates for the RIS technique. It

now seems that a major role of the technology will be the selective detection of molecules in science, industry and medicine.

For the application of RIS techniques to molecular species, the molecules must be prepared in a free state, and the 'hot band' rotational and vibrational contributions to their spectra eliminated. For non-volatile molecules such as chlorophyll, mesoporphrin and tripeptides, ultraviolet laser ablation can be used to introduce free molecules into a supersonic gas stream from a nozzle, thus cooling the molecules of interest and causing them to populate their lowest vibrational state (U. Bösel, Technical University, Munich). Other volatile molecules such as xylene isomers (R.J. Donovan, University of Edinburgh) and acetamide (E. Benedetti, University of Naples) can be simply evaporated into the nozzle gas stream. Acetamide is of interest as it is a basic component of peptides and proteins, whereas the ability to determine the relative amounts of different isomers of compounds such as xylene has important industrial applications.

An extraordinarily sensitive device has been developed that can detect and count 1,000 atoms in a background of  $10^{15}$  atoms of other krypton isotopes (N. Thonnard, Atom Sciences, Oak Ridge, Tennessee). The first application of this device will be to measure the quantity of  $^{85}\text{Kr}$  and  $^{87}\text{Kr}$  in hydrological, oceanographical and atmos-

pheric samples to date ground water and polar ice, and to determine circulation patterns in the deep ocean or the atmosphere. Another significant achievement is the measurement, on a production basis, of impurities with a high degree of reproducibility in semiconductor substrates at the  $10^{-9}$  level (J. Parks, Atom Sciences). Bioassays of trace elements and uranium can also be made with similar sensitivity using tiny samples of blood or urine. The medical applications are of great importance, as these are techniques which could provide rapid analysis of trace amounts of a wide variety of substances using very small samples. Small size also has the advantage of reducing the effect of reagent contamination on detection sensitivity when a chemical step is required.

The preparation of free sources of atoms for RIS measurements is being investigated both experimentally and theoretically (N. Winograd, Pennsylvania State University). Ion sputtering and electron and photodesorption of atoms indicates that both bond breaking and momentum transfer are effective mechanisms in producing free atoms from surfaces.

Various types of mass spectrometry are now being used together with RIS to improve selectivity. Descriptions were presented at the meeting of time-of-flight mass spectrometers, magnetic and electrostatic mass spectrometers and the 'Reflecton' device used to improve time-of-flight spectroscopy. Other techniques include double resonance, hyperfine structure discrimination and the use of synchronized pulsed-atom sources, detectors and lasers. Many of these techniques permit the analysis of very small samples including airborne particles, oil and blood samples, and others, allowing the detection of nanogram quantities of copper, uranium and other elements of interest. An RIS system is in use for geological and mineral exploration in China (Keling Wen, Quinghua University).

Isotope and isomer separation techniques now often involve RIS (for example, J.K. Crane, Lawrence Livermore National Laboratory). The presentations describing these techniques were limited to atomic vapour techniques to produce separations of isotopes, such as those of uranium and mercury, in large quantity although molecular techniques using flow cooling have also been demonstrated. If cost-effective, many isotopes could have great commercial value when produced in quantity in this way. One of the more exotic uses of RIS is in the search for quarks and heavy atoms, but the results to date are, unfortunately, negative. □

*Keith Boyer is Emeritus Professor at the Laboratory for Atomic, Molecular and Radiation Physics, College of Liberal Arts and Sciences, University of Illinois, Box 4348, Chicago, Illinois 60680, USA.*

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